Dawsonite Reactivity in Geologic Carbon Sequestration

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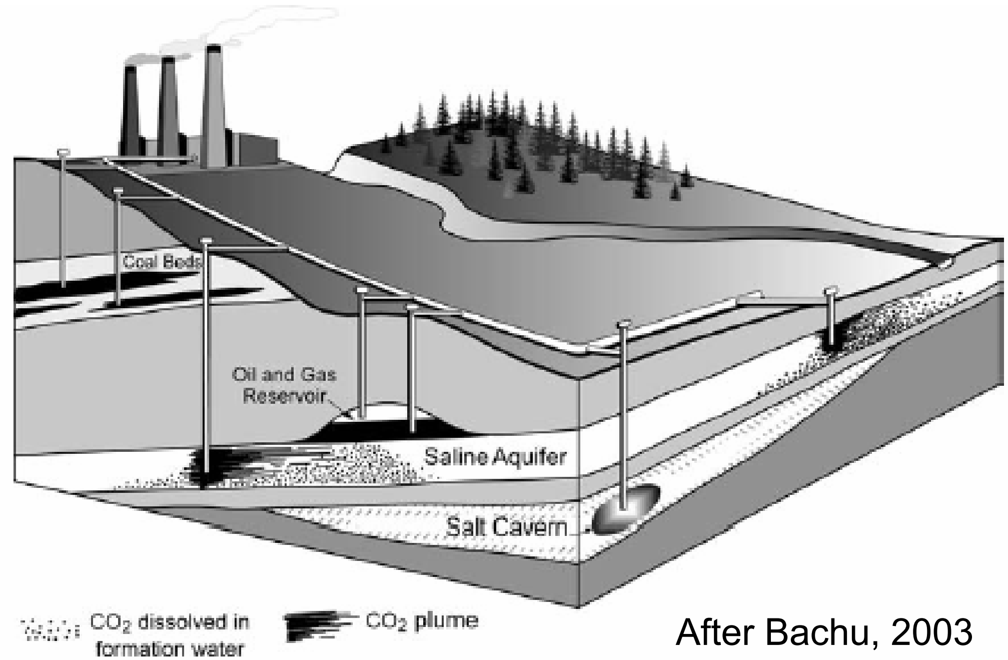
Mechanisms of Geologic Sequestration

- **Hydrodynamic trapping**
  - CO_2 trapped as supercritical fluid or gas under low-permeability caprock
  - Most important mechanism, in short term (?)
- **Solubility trapping**
  - CO_2 dissolved in brine
  - Reduces likelihood that CO_2 will return to atmosphere quickly



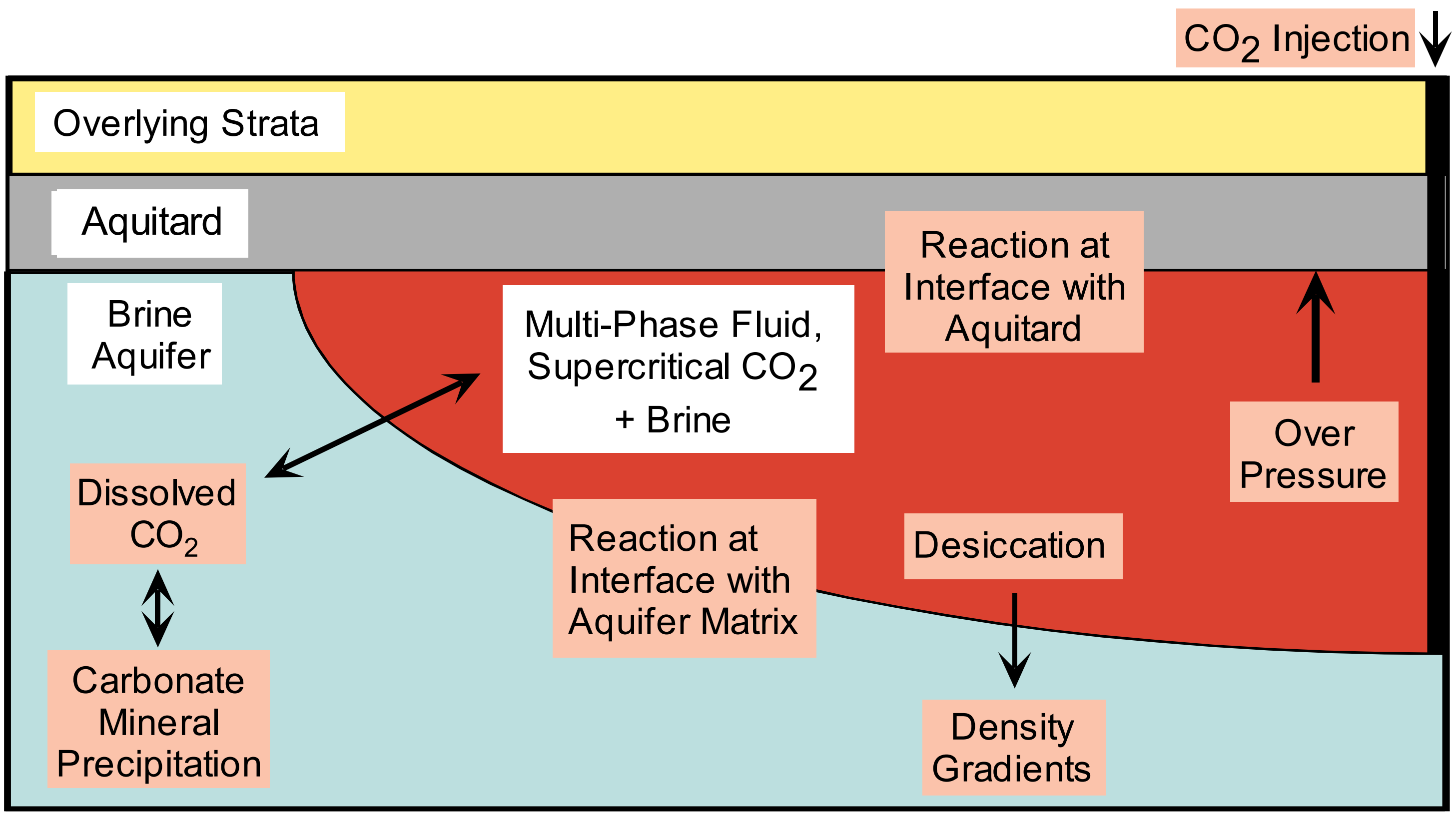
After Bachu, 2003

- **Mineral trapping**
  - Consume CO_2 by reaction with minerals
    - Precipitate carbonate minerals
    - Silicate reactions
  - The most permanent solution: stable repositories

Dawsonite ($NaAlCO_3(OH)_2$) Problem

- Numeric simulation – dawsonite important carbon-trapping mineral for carbon repositories.

- Rare in experiment and nature (reported occurrences numbering in the 10's of localities).



Today

- Background
- Approach
- General Results
  - Broad Summary and Conclusions
- Detailed results at poster
- Discussion

Dawsonite ($NaAlCO_3(OH)_2$)

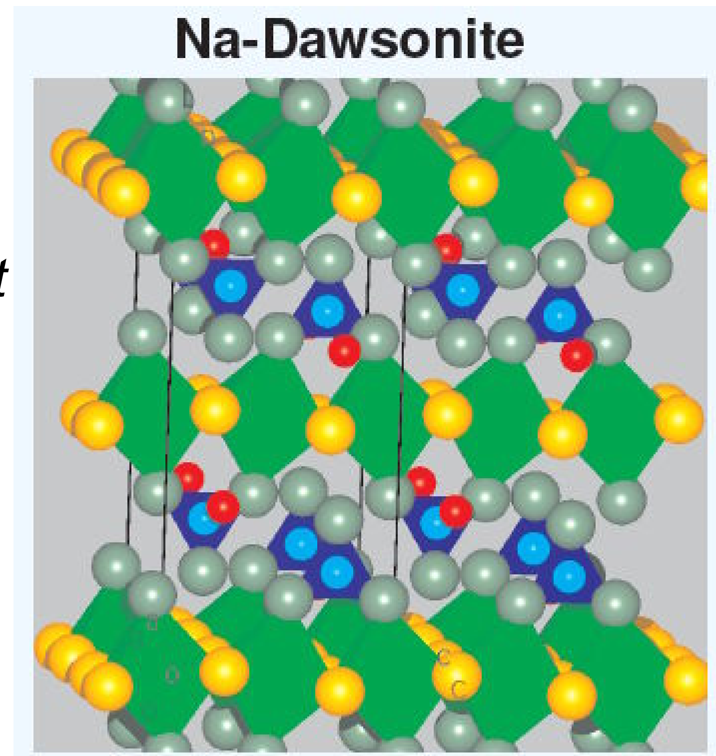
Na-Dawsonite (Imma)

K-Dawsonite and NH_4-Dawsonite (Cmcm)

No solid solution of Na- and K-phases

Occurrences

- saline, alkaline lacustrine basins, Green River Fm. (Hay 1964)
- Springerville–St. Johns CO_2 field (Moore *et al*., 2005)
- Permo-Triassic Bowen-Gunnedah-Sydney basin system, eastern Australia (Baker *et al*., 1995)
- Tin Mountain pegmatite, Black Hills, SD (Sirbescu and Nabelek, 2003)



Dawsonite ($NaAlCO_3(OH)_2$)

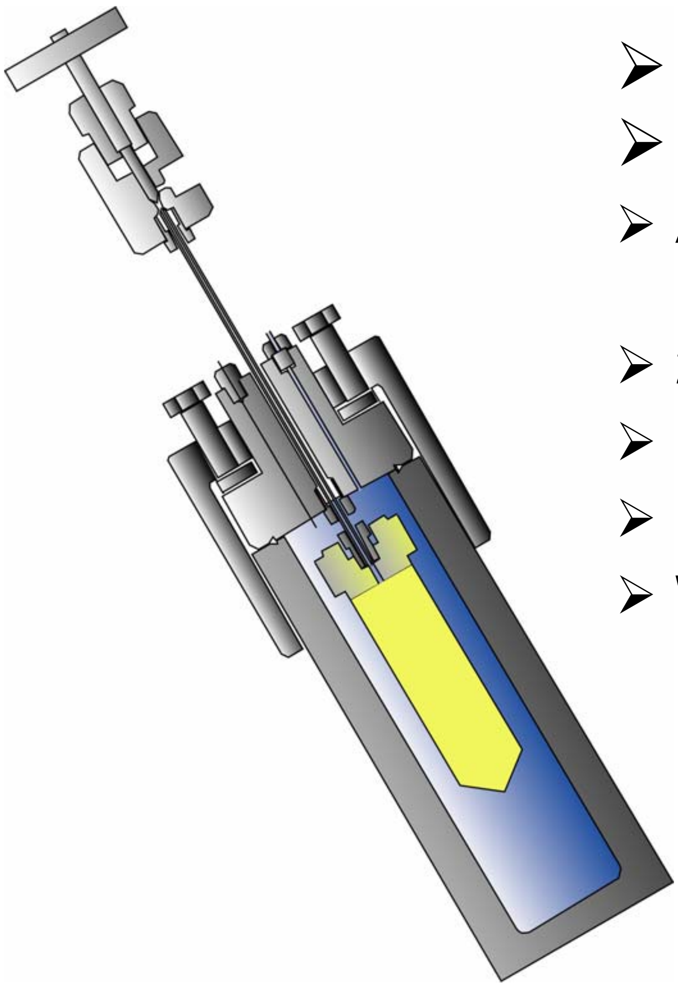
Only thermodynamic data: Ferrante *et al*., 1976, calorimetric investigation of synthetic dawsonite

Solubility experiments in DI water suggest these thermodynamic data correctly predict dissolution behavior (Duan *et al*., this meeting)

Kinetic dissolution experiments: Hellevang *et al*., 2005: dawsonite stability depends on P_{CO_2}

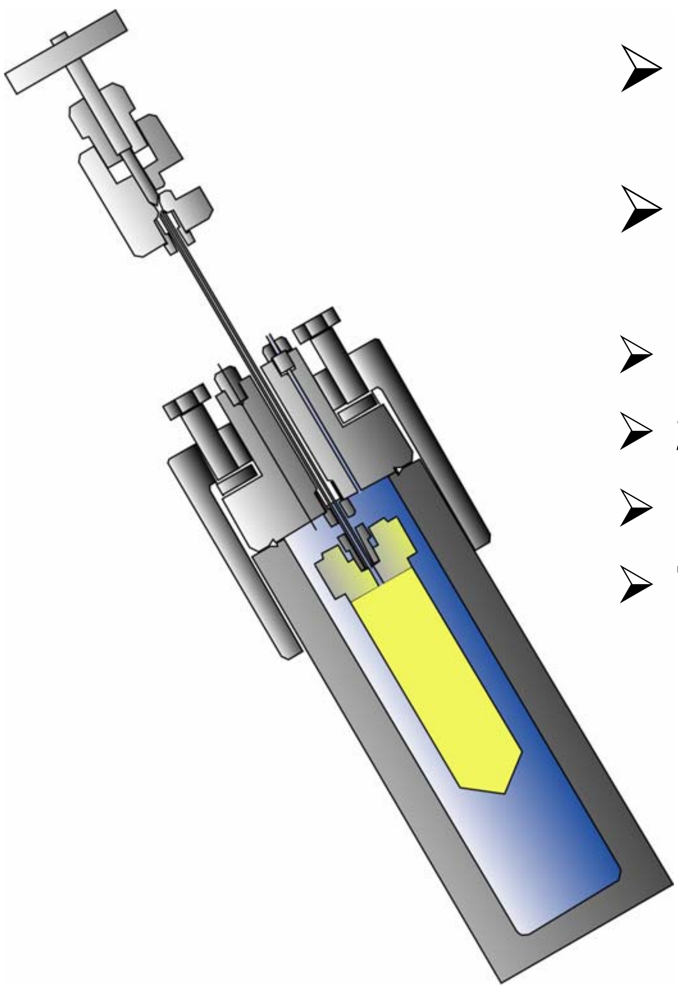
Experiments in geologically-relevant solutions suggest enhanced solubility (this meeting)

Synthesis Experiments



- Conditions that maximize reactivity *vs.* reservoir conditions
- Parr bombs, stirred autoclaves, rocker bombs
- NaCl, $NaHCO_3$, NaCl+$NaHCO_3$, NaCl+CO_2
- Al minerals: gibbsite, kaolinite, montmorillinite, albite, K-feldspar, zeolites
- 25 to 200°C
- 1 bar to reservoir pressures of 200 bar
- 1 to 180 days
- Water:Rock up to 125:1

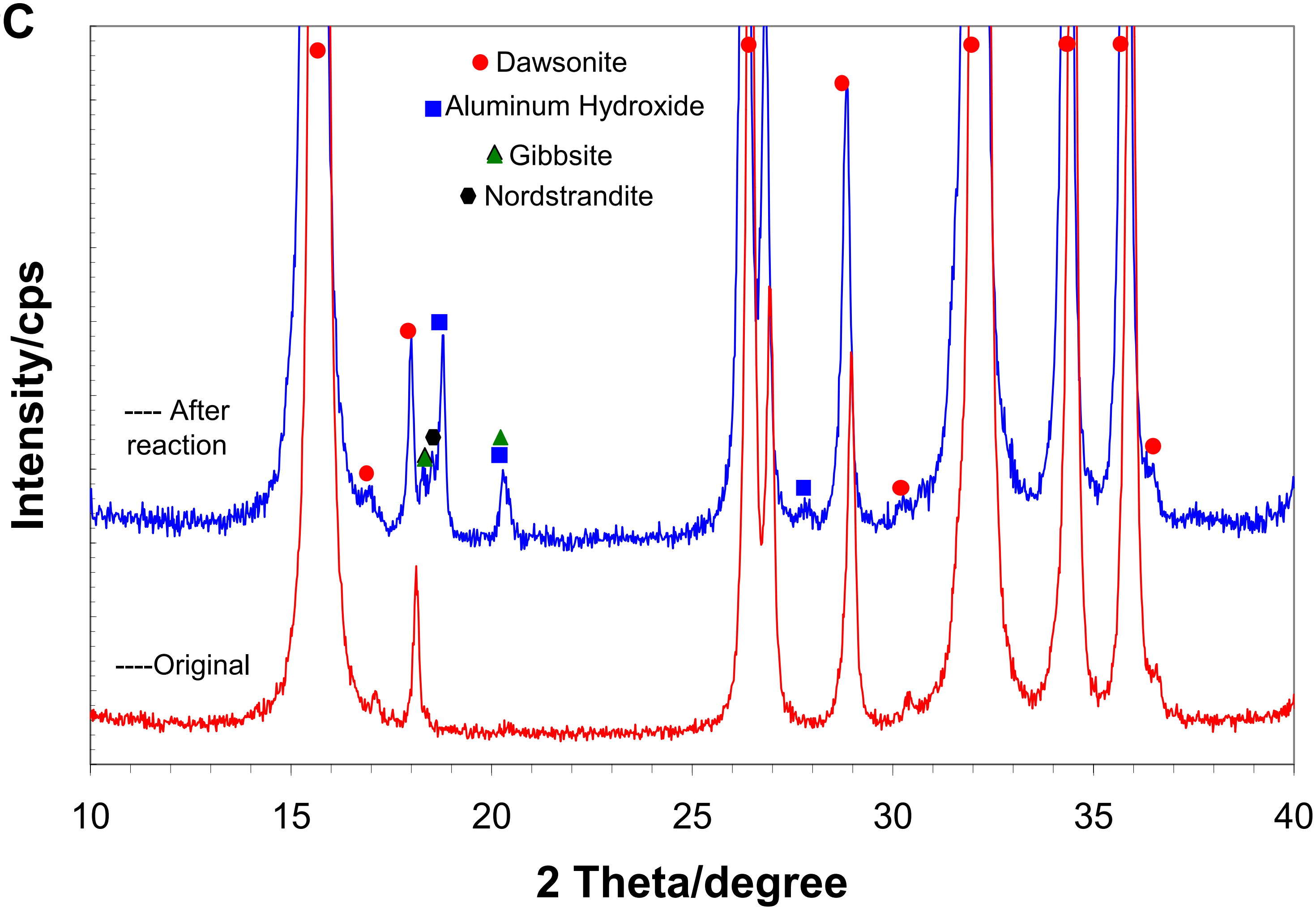
Dissolution Experiments



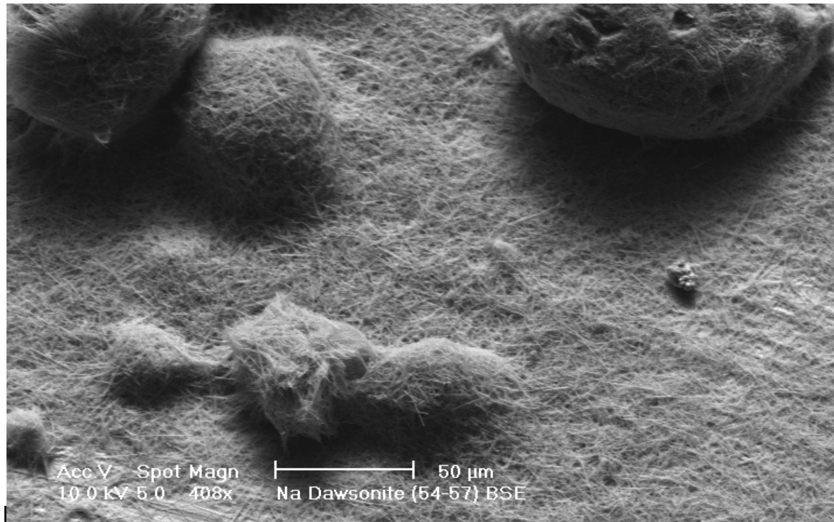
- Conditions that maximize reactivity *vs.* reservoir conditions
- Benchtop flow-through reactor and rocker bombs
- De-ionized H_2O, NaCl, $NaHCO_3$, pH=3 HCl, NaCl+CO_2
- Na- and K-dawsonite
- 25 to 75°C
- 1 bar to reservoir pressures of 200 bar
- 7 to 41 days

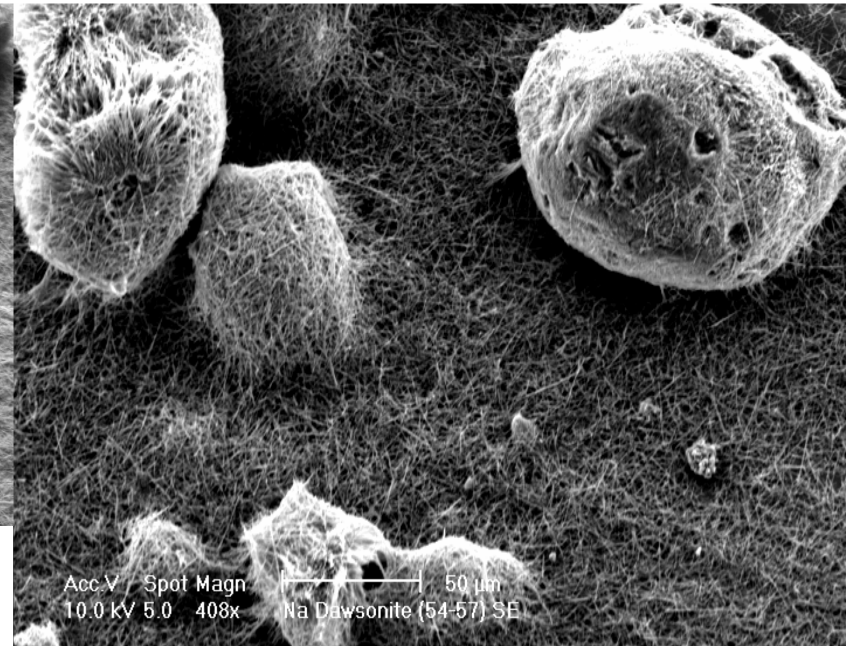
1. Dawsonite Readily Forms…

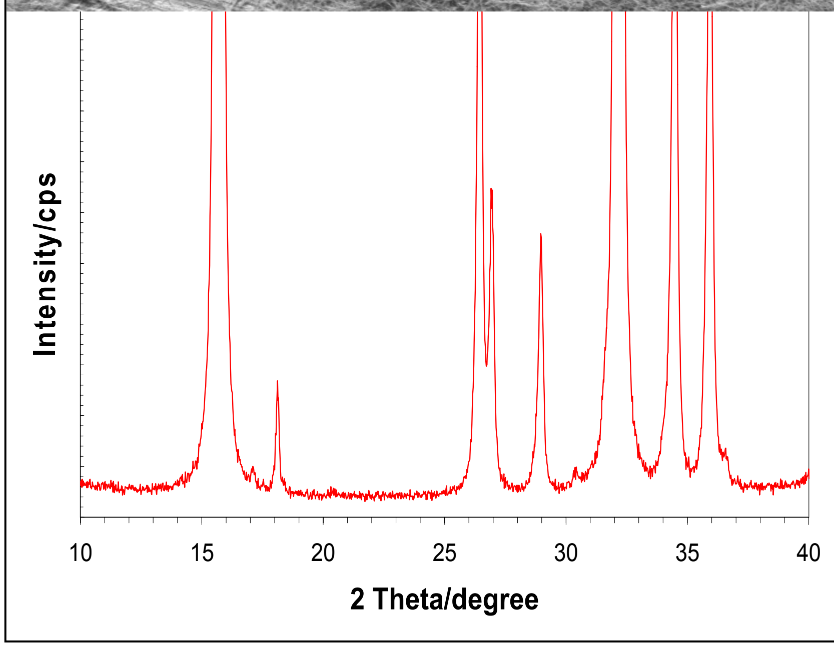
Systems with a reactive source of Al (reagent-grade gibbsite)
- **hours at 150°C**
- **months at 75°C**

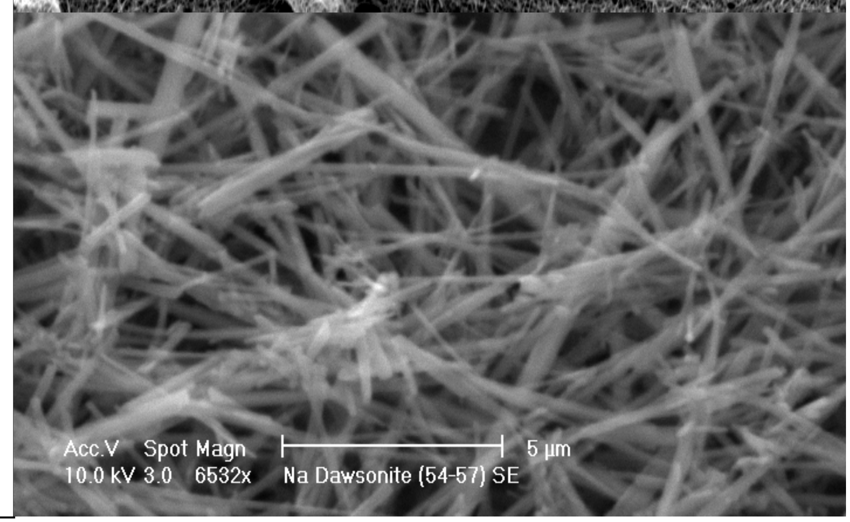


Dawsonite ($NaAlCO_3(OH)_2$)





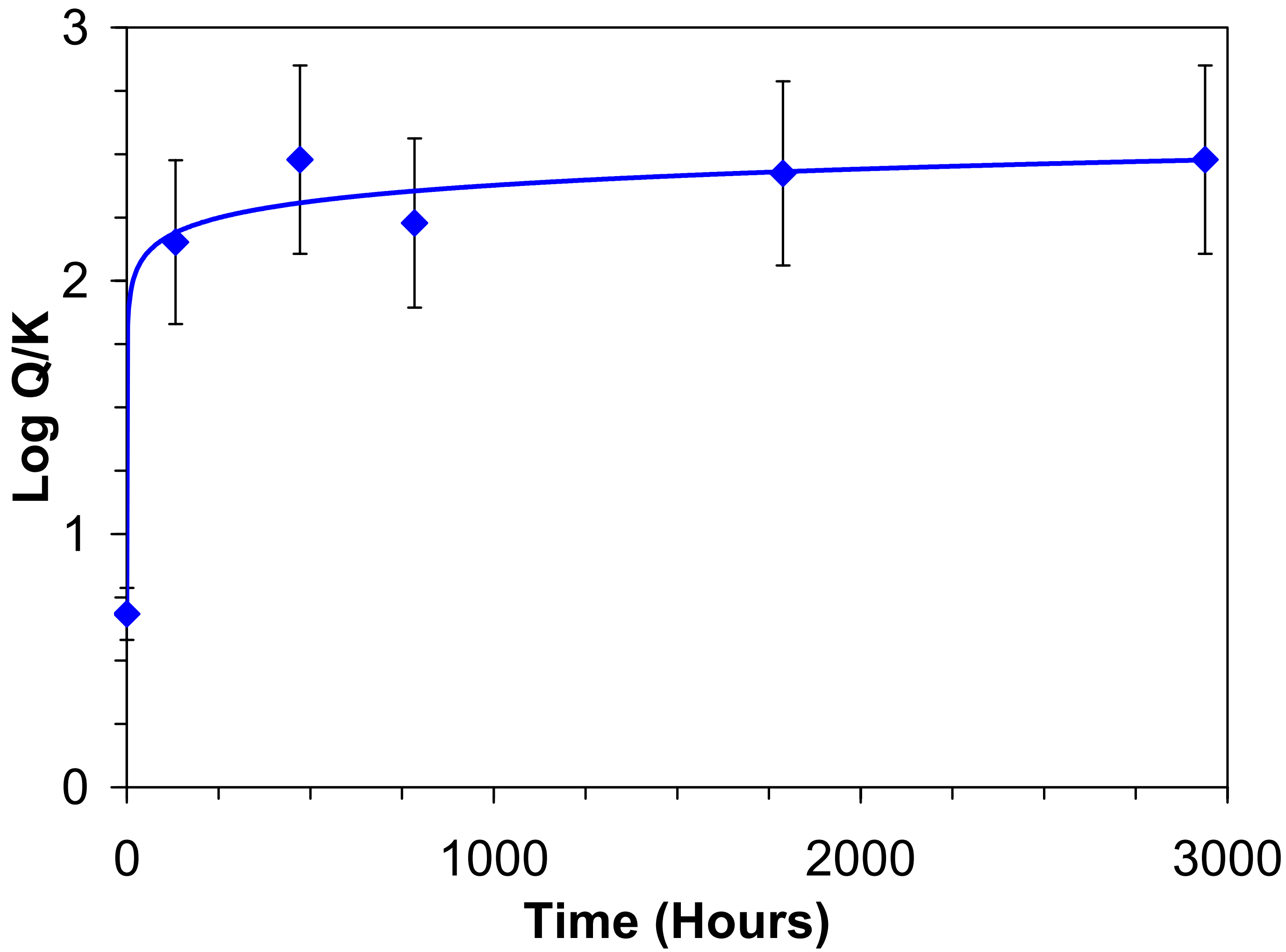




2. Dawsonite Forms Less Readily…

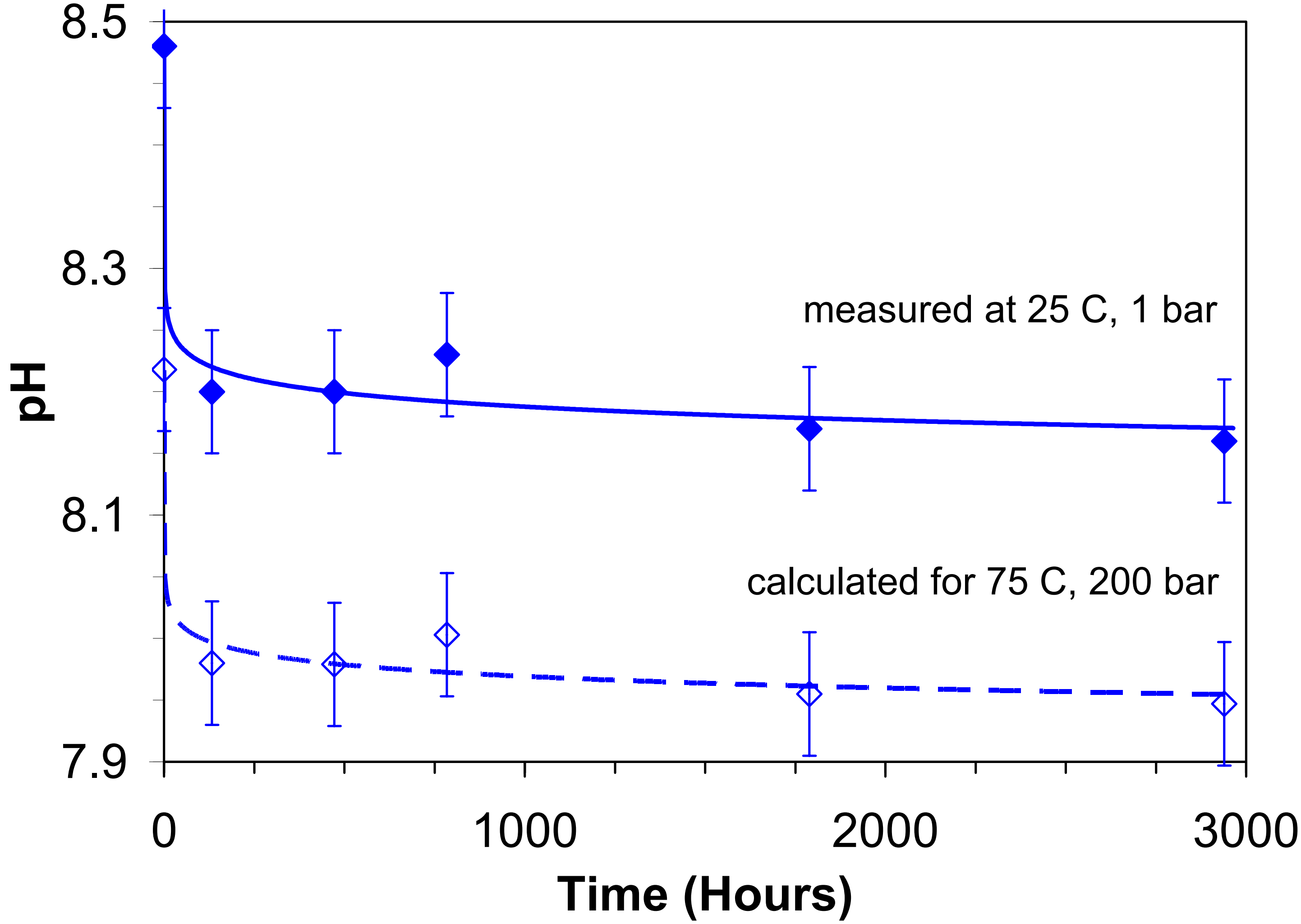
In systems with less reactive Al source

- **Kaolinite in $NaHCO_3$ at 75°C and 200 bars for 4.1 months**



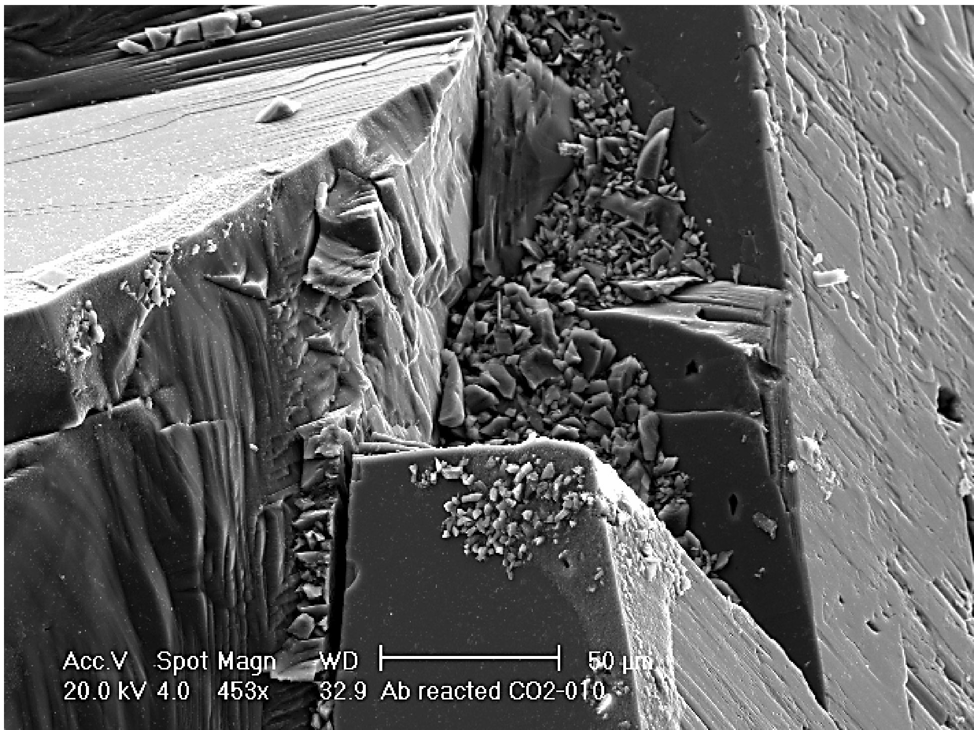
2. Dawsonite Forms Less Readily

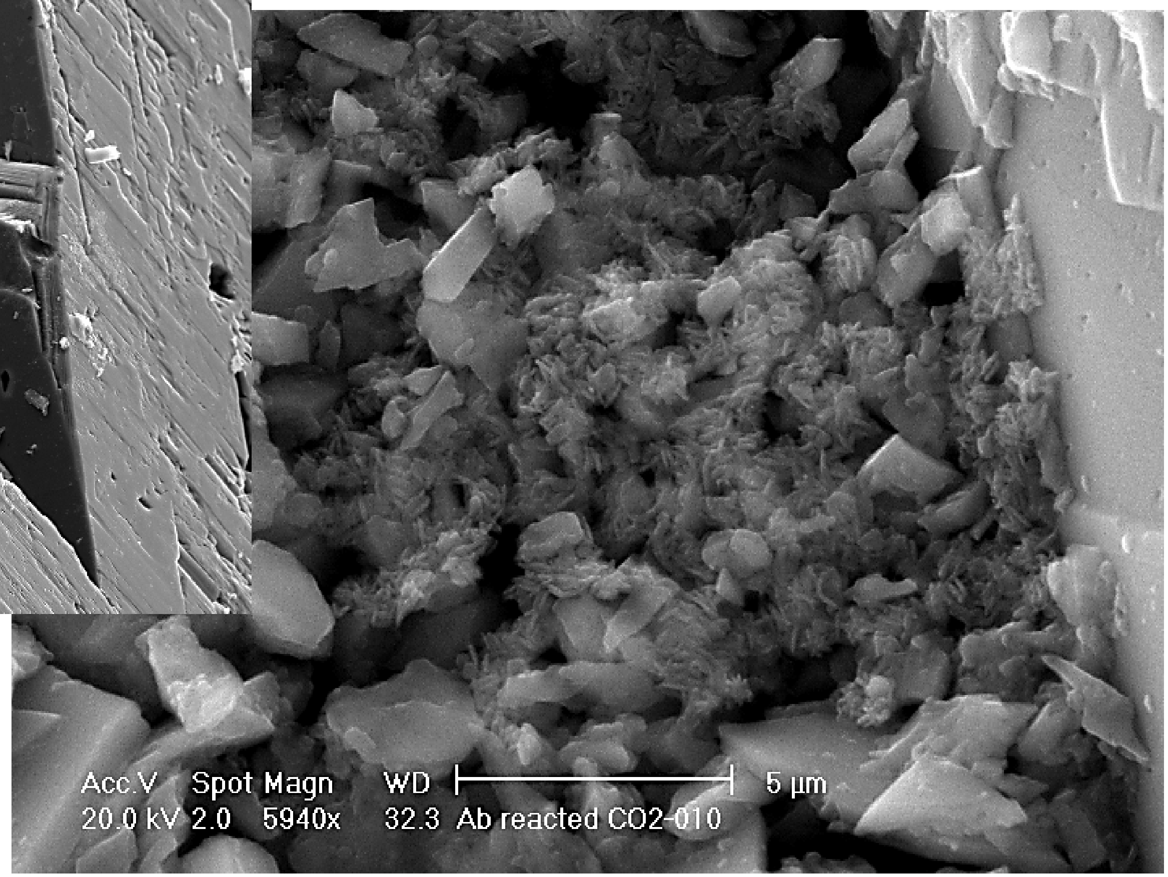
- $NaHCO_3$ buffers pH to ideal conditions for dawsonite precipitation
  - ➢ Yield = 0.2%



2. Dawsonite Forms Less Readily…

- Albite in NaCl + CO_2, 75°C, 200 bars for ~3 months
  - Yield = 0.0%



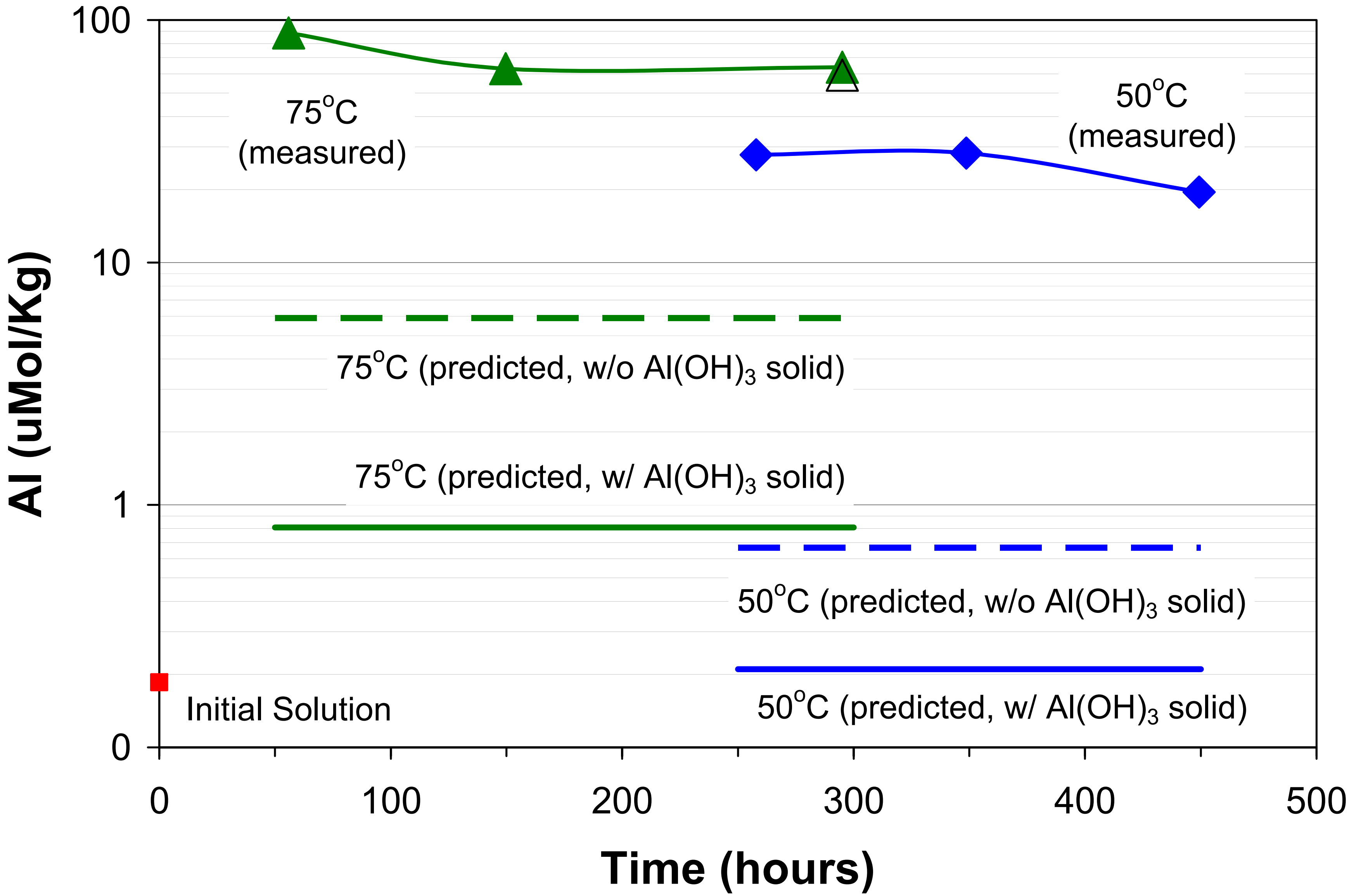


General Observations Regarding Dissolution

3. Dissolution in DI water is consistent with thermodynamic data

4. To date, dissolution in ionic solutions is not consistent with thermodynamic data.
   - Trends may indicate equilibrium for long term
   - Currently running long-term experiments

Dawsonite and Al in Solution



General Observations

1. Dawsonite forms readily in systems with reactive source of Al (reagent-grade gibbsite)

2. Dawsonite forms less readily in systems with less reactive Al source

3. Dissolution in DI water consistent w/ thermodynamic data

4. Dissolution in ionic solutions not consistent with thermodynamic data for expt's run to date.

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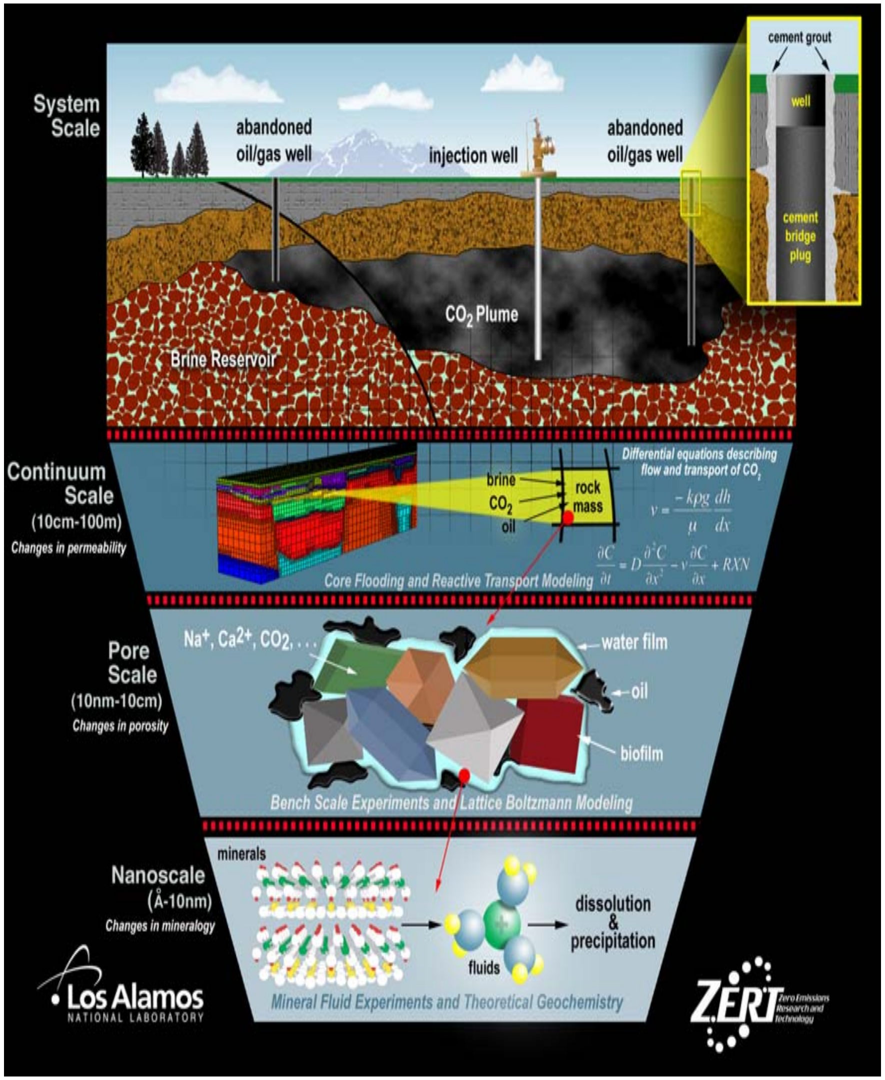

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While prominent in a host of modeling studies, dawsonite ($NaAlCO_3(OH)_2$) rarely occurs in nature and is not a precipitant in experimental simulations of a carbon repository. Given the potential importance of dawsonite to geologic carbon sequestration, the stability of this mineral requires critical examination. Short-term experiments demonstrate that dawsonite is readily synthesized from gibbsite and kaolinite in concentrated $NaHCO_3$ solutions. A series of hydrothermal fluid-mineral experiments were used to assess the long-term geochemistry and reactivity of dawsonite in more geologically reasonable solutions: moderately saline (0.05 molal) $NaHCO_3$ solution with synthetic dawsonite at 50 and 75°C, 200 bars; 1 molal $NaHCO_3$ brine with Georgia kaolinite and with albite at 75°C, 200 bars; and 1 molal NaCl brine with Georgia kaolinite and with albite at 75°C, 200 bars. In these last two experiments, the brine-mineral system was reacted at pressure and temperature to approach steady state, then injected with supercritical CO_2 and allowed to react an additional 60 days. Reacted fluid was periodically sampled and analyzed, for pH, CO_2, and elemental chemistry. Quench solids were also analyzed, and select samples were analyzed for colloidal particle-size-distribution and concentration. At temperature-pressure conditions expected for a carbon repository, dawsonite dissolves to yield 10-100 times more Al in $NaHCO_3$ solution than predicted using existing thermodynamic data. Kaolinite dissolves in $NaHCO_3$ to yield <1wt% dawsonite after ~3000 hours of reaction. Al-hydroxide colloids, a significant fraction of which are smaller than 0.45 microns, developed in solution. The colloidal fraction that is less than 0.45 microns, a commonly used filter size, accounts for at least some of this Al surplus. The Al surplus and the colloid abundance also appear to be related to the $NaHCO_3$ concentration. Formation of dawsonite in response to CO_2 injection is not as prolific as predicted by computer modeling of carbon repositories. We continue to evaluate the cause(s) for these discrepancies.

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References

Duan, Ren-Guan, Carey, J. William, and Kaszuba, John P., 2005, Mineral chemistry and precipitation kinetics of dawsonite in the geological sequestration of CO_2: Eos, Transactions, v. 86, no. 52, Abstract GC13A-1210.

Ferrante M. J., Stuve J. M., and Richardson D. W., 1976, Thermodynamic data for synthetic dawsonite: US Bureau of Mines Report of Investigations 8129, 13p.

Kaszuba, John P., Janecky, David R., and Snow, Marjorie G., 2003, Carbon dioxide reaction processes in a model brine aquifer at 200^{o}C and 200 bars: Implications for geologic sequestration of carbon: Applied Geochemistry 18 (7), 1065-80.

Kaszuba, John P., Janecky, D.R., and Snow, Marjorie G., 2005, Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and NaCl brine: Relevance to the integrity of a geologic carbon repository: Chemical Geology 217 (3-4), 277-93.